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Estimation of the Thermodynamic Properties of Several Oxygenated Compounds Involved in Biomasses Pyrolysis

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As already well established, the products of biomasses pyrolysis can be important in the exploration of alternatives to the use of fossil fuels. The study of the kinetic mechanism of thermal degradation of biomasses requires the knowledge of thermodynamic properties of the species, molecules and radicals, involved in the reaction path. These properties have been estimated by using the group contributions method and the program THERM. Particularly in the case of radicals the use of THERM can be difficult and, as an alternative, here is proposed a criterion based on analogy rules (isodesmic method). The obtained properties have been tabulated and compared with the experimental data where available. Moreover a comparison among the methods has been performed. A useful databank for several oxygenated compounds involved in biomasses pyrolysis has been obtained.

1. Introduction

In a continued search for higher performance, increased selectivity and faster development of new processes, accurate models describing the pyrolysis and combustion of biomasses are required. As well known these processes are besed on complex reaction systems involving radicals and hundreds of kinetically significant reaction intermediates. The development of a kinetic model based on elementary reactions is, therefore, challenging. Our research group, beside others (Susnow et al., 1997, De Witt et al., 2000, Green et al., 2001), has a long and successful history in this field (Dente et al., 1979, Dente et al., 2007, Calonaci et al., 2010). The development of these kinetic schemes requires the estimation of kinetic and thermodynamic parameters. Through the equilibrium constant of a reaction it is possible to deduce the direct or reverse kinetic constant once one of the two in known (for instance available on NIST or deduced by means of analogy rules with other similar reactions). It is therefore essential to have an appropriate tool for the estimation of thermodynamic properties. Despite the increasing computational power, the *ab-initio* calculation of kinetic and thermodynamic parameters for all the components is not realistic mainly for three reasons (Saeys et al., 2004). First, the number of involved reactions would require the evaluation of too many kinetic and thermodynamic parameters. Second, the discrepancy between experimental data and *ab-initio* calculation increases with the size of analyzed molecule or radical. Last, but not least, it is too much time consuming. In this paper different criteria, alternative to *ab-initio* calculations, are compared. They are based on the additivity of the properties of the molecule constituting groups. Firstly Benson's

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group contributions method (1960) has been proposed and adopted. Then the results have been compared with those obtained by the use of THERM. Finally, calculated properties have been compared with the experimental ones, when available (Handbook of Chemistry and Physics, referred as HB). In the case of radicals, the evaluation of properties is, in general, more difficult. Here a specific contribution is proposed by adopting a method similar to isodesmic calculations (Zhu and Bozzelli, 2003).

2. Method

Any group contributions method consists, of course, in the subdivision of the molecule in constituent groups, each of them contributing to the desiderated property. In practice, by defining as Y this property, it is simply evaluated by an addition rule:

$$Y = \sum_{i=1}^{GN} n_i B_i \qquad (1)$$

where B_i is the contributions of group "i" on the total number of groups GN, and n_i is the group occurrence inside the molecule. A sufficiently complete database for group contributions evaluation has been given by Benson (1960). This method can be also applied to radicals, however the database in this case is lacking of informations. Benson (1960) reported only some more diffused radical groups. For the characterization of the radical properties, it is not sufficient to evaluate just the contribution of the group containing the unpaired electron, but also how the adjacent groups are influenced by the presence of the radical position. It is therefore evident that the number of group contributions necessary is larger than that usually available in the literature. Consequently it has been necessary to find a way for solving the problem. A first solution seems to be to use the program THERM (Ritter and Bozzelli, 1991). It allows to evaluate the thermodynamic properties ($\Delta H°$, $S°$, Cp) of molecules and radicals and it is based on the use of group contributions method. Moreover entropy evaluation is based on the evaluation of the numbers of rotors and of symmetries of the molecule or radical. The database of THERM contains also that of Benson but in the case of radicals properties evaluation it is more extended. If also THERM doesn't contain a specific group, a method similar to isodesmic calculations can be used. It can be applied only for the evaluation of ΔH_f. It consists in using the group contributions method for evaluating the ΔH_f of a molecule and in deducing the properties of the derived radical by addition of a contribution deduced from the analogy with a similar but known molecule and radical.

Figure 1: structure of ($C_5H_3O_2$) and ($C_4H_5O_3$) radicals

In order to better clarify the procedure, the following two examples are reported. In figure 1 are depicted the two radicals considered for the properties evaluation.

Table 1: Calculation of the ΔH_f *of* $C_5H_4O_2$ *and molecule*

$C_5H_4O_2$ Groups	H_f Kcal/mole (300°C)
Cd(Cd)(H) x 2	6.78 x 2
Cd(O)(H)	8.6
Cd(O)(CO)	11.6
O(Cd_2)	-33.0
CO(Cd)(H)	-29.1
C_5 cycle	-5.8
Sum ($C_5H_4O_2$)	-34.14
$C_4H_6O_3$ Groups	H_f Kcal/mole (300°C)
CO(O)(Cd)	-32.0
O(CO)(H)	-58.1
Cd(CO)(H)	5.0
Cd(H)(C)	8.59
C(Cd)(O)(H_2)	-6.5
O(H)(C)	-37.9
Sum ($C_4H_6O_3$)	-120.91

Radical $C_5H_3O_2$:

IDRC: ΔH_f ($CH_2CHC\bullet O$) – ΔH_f (CH_2CHCHO) = 21.2 + 17.8 = 39 kcal/mol

ΔH_f ($C_5H_3O_2$) = ΔH_f ($C_5H_4O_2$) + IDRC = -34.14 + 39 = 4.86 kcal/mol

Radical $C_4H_5O_3$:

IDRC: ΔH_f ($CH_3CH_2O\bullet$) – ΔH_f (CH_3CH_2OH) = - 3.25 + 56.09 = 52.84 kcal/mol

ΔH_f ($C_4H_5O_3$) = ΔH_f ($C_4H_6O_3$) + IDRC = -120,91 + 52,84 = -68,07 kcal/mol

The evaluation takes into account the kind of bond that is broken, and the atoms and bonds of the adjacent positions starting from the unpaired electron. For instance the contribution of an H atoms of a carboxylic acid differs from the of an alcoholic group, because of the presence of oxygen in α position, causing electron partial shift towards the terminal hydroxyl.

3. Comparisons of the results obtained with the three methods

The experimental data for molecules and radicals are related mainly to ΔH_f (ΔS_f and specific heat are rarely available). The isodesmic method (IDRC) is particularly convenient for evaluating the ΔH_f. Therefore the following comparisons will regard only the enthalpy of formation. Table 2 reports a first comparison between experimental ΔH_f and the ones calculated by using THERM. For other radicals, when experimental data are not available, a comparison among the three methods is reported (Table 3).

Table 2: Comparison between experimental data (Hand Book, HB) and THERM

	ΔH_f (298K) HB	ΔH_f (298K) THERM	Deviation
$C_2H_5^{\bullet}$	28.38	29.00	0.62
$C_6H_5^{\bullet}$	78.86	79.82	0.96
$C_6H_5CH_2C^{\bullet}H_2$	56.38	56.15	-0.23
$CH_3CH^{\bullet}OH$	-12.90	-11.60	1.3
$^{\bullet}CH_2CH_2OH$	-7.41	-7.00	0.41
$CH_3CH_2C^{\bullet}O$	-7.57	-7.40	0.17
$CH_3COCH_2^{\bullet}$	-8.12	-9.26	-1.14
$C_6H_5COOCH_2^{\bullet}$	-16.70	-20.50	-3.8
$C_2H_5O^{\bullet}$	-4.04	-4.04	0.
$C_6H_5O^{\bullet}$	11.59	12.10	0.51
$C_6H_5CH_2O^{\bullet}$	32.49	29.31	-3.18
$CH_3COO^{\bullet}$	-42.98	-43.38	-0.4

Table 3: enthalpy of formation of radicals with different methods: ΔH_f (298K)

	IDRC	Benson GC	THERM
$[C_4H_3O]C^{\bullet}O$	1.24	1.17	0.76
$CH_3CH_2O^{\bullet}$	-4.03	-4.1	-4.04
$CH_2^{\bullet}CH(OH)_2$	-53.52	-56.28	-52.8
$HOCH_2CH_2O^{\bullet}$	-39.84	-40.6	-40.04
$CH_2^{\bullet}CH_2^{\bullet}$	73.24	79.85	75.21
$O^{\bullet}CdHCdHCH_2^{\bullet}$	46.5	42.45	47.42
$CH_3CH_2C^{\bullet}O$	-7.26	-10.5	-7.4
$CH_2^{\bullet}COCH_2$	-43.77	-41.58	-43.58
$CH_3COCH_2O^{\bullet}$	-35.44	-35.5	-33.92
$OH(C_dH)_2CH_2C^{\bullet}O$	-19.3	-21.08	-23.28
$O^{\bullet}CH_2(CdH)_2CHO$	-7.75	-8.56	-8.89

Table 4: Deviations of THERM and GC with respect to IDRC method

	IDRC	GC	THERM	GC-IDRC(%)	THERM-IDRC (%)
$[C_4H_3O]C^{\bullet}O$	1.24	1.17	0.76	-0.07	-0.48
$CH_3CH_2O^{\bullet}$	-4.03	-4.1	-4.04	-0.07	-0.01
$CH_2^{\bullet}CH(OH)_2$	-53.52	-56.28	-52.8	-2.76	0.72
$HOCH_2CH_2O^{\bullet}$	-39.84	-40.6	-40.04	-0.76	-0.2
$CH_2C^{\bullet}CH_2O^{\bullet}$	73.24	79.85	75.21	6.61	1.97
$O^{\bullet}CdHCdHCH_2^{\bullet}$	46.5	42.45	47.42	-4.05	0.92
$CH_3CH_2C^{\bullet}O$	-7.26	-10.5	-7.4	-3.24	-0.14
$CH_2^{\bullet}COCH_2OH$	-43.77	-41.58	-43.58	2.19	0.19
$CH_3COCH_2O^{\bullet}$	-35.44	-35.5	-33.92	-0.06	1.52
$OH(CdH)_2CH_2C{\bullet}O$	-19.3	-21.08	-23.28	-1.78	-3.98
$O^{\bullet}CH_2(CdH)_2CHO$	-7.75	-8.56	-8.89	-0.81	-1.14
AVERAGE				-0.44	-0.06

Table 4 shows the deviation of Benson GC method and THERM with respect to IDRC method. The major deviations can be observed with respect to GC method, probably because Benson contributions work better for small radicals and molecules. From the table it can be observed that IDRC method can be alternative to the use of THERM. The average deviation has been found to be of -0.44 and -0.06 (in general a difference of ± 2 kcal is acceptable). Table 5 reports only some of the obtained results for lacking of space (the enthalpy of formation of 119 radical has been calculated and the results can be requested directly to the authors of this paper).

*Table 5: Results obtained with the three methods ([ ] brackets refer to IDRC, * refers to THERM, number without label refers to Benson GC)*

	Formula and name	ΔH_f(298)[Kcal/mol]	ΔS_f(298)[cal/mol]	cp[cal/mol/K]
	$C_2H_5O_2$ (1-hydroxyethyl) oxidanyl	-50,3 -49,84*	78 76,1 72,73*	19,06*
	$C_2H_5O_2$ 2,2-dihydroxyethyl	-54,6 [-56,28]	83 [77,84]	[19,39]
	$C_2H_5O_2$ 1,1-dihydroxyethyl	-61,2 -57,4*	76,2 79,43*	19,26*
	$C_2H_5O_2$ (2-hydroxyethyl) oxidanyl	-40 [-40,6]	78 [75,27]	[17,19]
	$C_2H_5O_3$ (1,1-dihydroxyethyl) oxidanyl	-71,2 -90,74*	84,6 80,31*	22,44*
	$C_2H_5O_3$ (1,2-dihydroxyethyl) oxidanyl	-86,1 -85,84*	86 83,48*	22,16*
	$C_3H_3O_3$ 2-hydroxy-1,3-dioxopropan-2-yl	-62,8 -58,37*	88 92,31*	21,79*
	$C_3H_3O_3$ (1,3-dioxopropan-2-yl)oxidanyl	-51,4 -50,81*	88 85,61*	21,58*
	$C_3H_3O_3$ [(1*E*)-2-hydroxy-3-oxoprop-1-en-1-yl]oxidanyl	-32,7 -47,98*	109,1 81,74*	24,22*
	C_3H_4O	79 [79,85]	76,5	17,61*
	C_3H_4O	[42,45]	75,5 75,18*	17,29*
	C_3H_6O 2-oxopropyl	-6 [-5,78]	71,5 [76,11]	[17,78]

	Formula and name	ΔH_f(298)[Kcal/mol]	ΔS_f(298)[cal/mol]	cp[cal/mol/K]
	C_3H_7O propan-2-yloxidanyl	-13 [-12,6]	71,8 [75,52]	[20,08]
	$C_3H_7O_2$ 2-hydroxy-2-methoxyethyl	-52 [-51,66]	89,5 [87,86]	[24,68]
	$C_3H_7O_2$ 2,2-dihydroxypropyl	-68,8 [-68,78]	89 [85,69]	[25,1]
	$C_3H_7O_2$ 1-hydroxy-1-methoxyethyl	-57,2 -52,7*	86,4 87,15*	24,55*
	$C_3H_7O_2$ (1-hydroxyethoxy) methyl	-52 [-54,32]	89,5 [87,86]	[24,68]
	$C_3H_7O_2$ 1-hydroxy-1-methoxyethyl	-61,3	90	
	$C_3H_7O_2$ (2-hydroxypropan-2-yl)oxidanyl	-62,6	82 79,73*	23,80*
	$C_3H_7O_2$ (1-hydroxypropan-2-yl) oxidanyl	-49,3 [-48,4]	88,6 [83,98]	[23,89]
	$C_3H_7O_3$ (1,2-dihydroxypropan-2-yl)oxidanyl	-98,6	95 90,49*	26,90*
	C_4H_5O furan-2-yl	49 43,62*	67,3 63,79*	14,76*
	$C_4H_3O_2$ 5-oxo-2,5-dihydrofuran-2-yl	-27 -18,98*	74 76,88*	18,36*
	$C_4H_4O_2$	5,8 12,03*	93 91,61*	24,44*

Also a comparison with the Burcat collection databank (Burcat and Ruscic, 2005) has been performed when possible and the data are in line with those reported into the HB collection. The major part of radicals here reported are not contained in the Burcat collection and a comparison is not possible.

4. Discussion and Conclusions

From the reported comparisons and the other analyzed data it can be observed that the more complex structures, containing aromatic rings and multiple bonds, present the higher deviations. Probably, this is due to the fact that the groups are ibridated sp2 producing a stabilizing resonance not taken into account. The IDRC can be used for the evaluation of the enthalpy of formation of more complex radicals offering reliable results, while GC and THERM are more convenient for the entropy and specific heat

calculation. Finally, it is worth to say that IDRC method, because of its simplicity, can be used for quickly verify the results obtained with the other methods.

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